

**REMARKS**

**I. Status of the Claims**

Claims 14-24 are pending. No claims have been amended by this response.

**II. 102(e)/103 Rejection**

The Examiner rejected claims 14-24 under 35 U.S.C. §§ 102(e)/103 as being anticipated by, or in the alternative, obvious in view of U.S. Patent No. 6,129,755 to Mathis et al. ("Mathis").

Applicant submits that Mathis neither anticipates the present claims nor renders the claimed invention obvious and requests reconsideration and withdrawal of the rejection for at least the following reasons. Since the Examiner has rejected the present claims under 102(e)/103, Applicant addresses both anticipation and obviousness in the following remarks.

**A. Anticipation**

With regard to claim 14, the Examiner alleges that "[t]he unrestrained portion free from sheath 40 is heated by the body temperature to a temperature in the range of 24-37 degree Celsius to be transformed into an austenite state as recited in the claim." Final Office Action at page 2.

To anticipate a claim, the reference must teach every element of the claim. M.P.E.P. § 2131; *Verdegaal Bros. v. Union Oil Co. of California*, 2 U.S.P.Q.2d 1051, 1053 (Fed. Cir. 1987) ("A claim is anticipated only if each and every element as set forth

in the claim is found, either expressly or inherently described, in a single prior art reference.”).

The disclosure of Mathis clearly does not teach each and every element set forth in the claims. Mathis discloses that “the stent is then cooled until it is completely martensitic, crimped down to its un-expanded diameter and then loaded into the sheath of the delivery apparatus.” Mathis at col. 9, lines 5-7. In the “Background of the Invention” section, Mathis discusses the characteristics of shape memory alloys and discloses that “heating of the deformed martensite phase to a temperature above the martensite to austenite transformation temperature causes the deformed martensite phase to transform to the austenite phase” but that “[i]f restrained, the metal will remain martensitic until the restraint is removed.” *Id.* at col. 2, lines 49-65.

The Examiner suggests that in a partially deformed configuration, the unrestrained portion of the stent free from the sheath may be transformed into an austenite phase. Final Office Action at pages 2 and 3. Contrary to the Examiner’s allegations, however, Mathis does not disclose when, or even if, the stent transforms from the martensite phase to the austenite phase. Moreover, Mathis never discloses a partially deformed configuration in which the unrestrained portion may be in the austenite phase. Mathis discloses that the stent is cooled until it is “completely martensitic” and then crimped. Mathis at col. 9, lines 5-7. Furthermore, as Figure 2 of Mathis clearly shows, the entire crimped stent 50 is restrained by the sheath 40, which runs the entire length of the stent. Therefore, the Examiner’s assertion that the stent of Mathis exists in a partially deformed state wherein the unrestrained portion is in the

austenite phase is mere conjecture at best because Mathis never discloses such a situation.

Thus, Mathis does not teach a medical device and delivery system having the elements recited in the present claims because Mathis does not teach a shape memory alloy element being in an austenitic state when in an at least partially deformed configuration in its restrained shape.

Regarding claim 23, the Examiner alleges that the stent and sheath/constraint of Mathis “comprise every structural limitation as recited in the claims and because the composition of stent 50 is in the range of the composition of the stent as claimed in the present invention, stent 50 must have martensite deformation temperature about 50 degrees C higher than  $A_f$  as recited in claim 23 of the present invention.” Final Office Action at page 3.

First, it is noted that the present claims do not recite a range of the composition, as stated by the Examiner. Furthermore, claim 23 and the claims from which it depends do not recite the components which comprise the shape memory alloy. Thus, the Examiner is improperly reading limitations into the claims.

Second, the Examiner states that the stent of Mathis “must have [a] martensite deformation temperature about 50 degrees C higher than  $A_f$ .” Final Office Action at page 3. The Examiner, however, does not provide any factual evidence or identify any teaching to support this allegation. The Examiner uses the phrase “must have” in the rejection, which means the Examiner is making an inherency argument.

To establish inherency, the Examiner must show that the alleged characteristic is necessarily present. M.P.E.P. § 2112; *Ex parte Levy*, 17 U.S.P.Q.2d 1461, 1464 (Bd.

Pat. App. & Inter. 1990) ("In relying upon the theory of inherency, the examiner must provide a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art." (emphasis in original)). The fact that a certain result or characteristic may occur or be present in the prior art is not sufficient to establish the inherency of that result or characteristic. *In re Rijckaert*, 9 F.3d 1531, 1534, 28 U.S.P.Q.2d 1955, 1957 (Fed. Cir. 1993) (emphasis in original).

The Examiner has not provided any evidence or technical reasoning to show why the nickel-titanium alloy used in the stent of Mathis necessarily has a martensite deformation temperature about 50 degrees C greater than the austenite finish temperature.

Furthermore, those skilled in the art recognize that the characteristics of shape memory alloys, including the martensite deformation temperature and austenite finish temperature, vary widely depending on the composition. For example, Melton, in "Ni-Ti Based Shape Memory Alloys," *Engineering Aspects of Shape Memory Alloys* (1990), pp. 21-35 ("Melton"), teaches that it is necessary to control the composition of nickel-titanium alloys to one-tenth to one-hundredth of a percent to achieve the desired transformation temperature. Melton at 23. As seen in Figure 2 of Melton, the transformation temperature can vary more than 100 degrees C by changing the amount of nickel in the alloy by about 2%. *Id.*

Because the characteristics of shape memory alloys change drastically with even a small change in the composition of the alloy, Applicant respectfully submits that the

Examiner has not met the burden required by the M.P.E.P. to show that the alleged characteristic is necessarily present.

For at least the foregoing reasons, Applicant submits that Mathis does not anticipate the claims and respectfully requests reconsideration and withdrawal of the rejection.

**B. Obviousness**

The Examiner further alleges that “[a]ternatively, it would have been obvious to one of ordinary skill in the art to select the exact composition of Ni and Ti within the range of 50.5%-60% Ni and the balance of Ti so as to stent 50 comprising every feature as recited in the claims.” Final Office Action at page 3.

As an initial matter, it is not clear why the Examiner is basing this obviousness rejection on a nickel-titanium alloy since claim 14 is not limited to such an alloy, and certainly not one having the ranges relied on by the Examiner. Rather, independent claim 14 is directed to a medical device and delivery system comprising any shape memory alloy. For this reason alone, the Examiner’s position is fundamentally flawed, thus rendering this rejection improper.

Even if the Examiner’s position on the nickel-titanium alloy was accurate, which it clearly is not, the Examiner has not established a *prima facie* case of obviousness showing why the claimed martensite deformation temperature would have been obvious to one skilled in the art based on the broad composition range of a nickel-titanium alloy disclosed by Mathis.

The initial burden is on the Examiner to provide some suggestion of the desirability of doing what the inventor has done. M.P.E.P. § 2142; *Ex parte Clapp*, 227 U.S.P.Q. 972, 973 (Bd. Pat. App. & Inter. 1985) ("To support the conclusion that the claimed invention is directed to obvious subject matter, either the references must expressly or impliedly suggest the claimed invention or the examiner must present a convincing line of reasoning as to why the artisan would have found the claimed invention to have been obvious in light of the teachings of the references.").

Obviousness can only be established by combining or modifying the teachings of the prior art to produce the claimed invention where there is some teaching, suggestion, or motivation to do so found either explicitly or implicitly in the references themselves or in the knowledge generally available to one of ordinary skill in the art. M.P.E.P. § 2143.01. Furthermore, to establish *prima facie* obviousness of a claimed invention, all the claim limitations must be taught or suggested by the prior art. *In re Royka*, 490 F.2d 981, 180 U.S.P.Q. 580 (C.C.P.A. 1974).

The Examiner has provided no motivation or teaching in the art to show why the claimed invention would have been obvious to one skilled in the art. Thus, the Examiner has failed to establish a *prima facie* case of obviousness as required by the case law.

Furthermore, Mathis teaches away from the claimed invention. Present claim 14 recites, *inter alia*, a shape memory alloy element "having been at least partially deformed at or above  $M_d$  into an at least partially deformed configuration" and "the shape memory alloy element being in an austenitic state when in the at least partially deformed configuration." In contrast, Mathis teaches a nickel-titanium stent that is

“cooled until it is completely martensitic, crimped down to its un-expanded diameter and then loaded into the sheath of the delivery apparatus.” Mathis at col. 9, lines 5-7. Thus, one skilled in the art would not be motivated to substitute the crimped martensitic stent of Mathis with a crimped austenitic stent.

The Examiner further suggests that it would have been obvious to one skilled in the art to select the exact composition of nickel and titanium within the range of 50.5% to 60% nickel. Final Office Action at page 3. Again, it is not clear why the Examiner is focusing on this specific alloy since the claimed invention is clearly not so limited.

Regarding ranges, the M.P.E.P. states that a range disclosed in a prior art reference that encompasses a narrower range may be sufficient to establish a *prima facie* case of obviousness. M.P.E.P. § 2144.05; *In re Peterson*, 315 F.3d 1325, 1330, 65 U.S.P.Q.2d 1379, 1382-83 (Fed. Cir. 2003). The M.P.E.P., however, conditions this statement by further stating that if the reference's disclosed range is so broad as to encompass a very large number of possible distinct compositions, this might present a situation analogous to the obviousness of a species when the prior art broadly discloses a genus. M.P.E.P. § 2144.05; *In re Peterson*, 315 F.3d 1325, 1330, 65 U.S.P.Q.2d 1379, 1382-83 (Fed. Cir. 2003).

To establish a *prima facie* case of obviousness in a genus-species chemical composition situation, as in any other 35 U.S.C. 103 case, it is essential that Office personnel find some motivation or suggestion to make the claimed invention in light of the prior art teachings. M.P.E.P. § 2144.08; *In re Brouwer*, 77 F.3d 422, 425, 37 U.S.P.Q.2d 1663, 1666 (Fed. Cir. 1996).

As explained above, the characteristics of shape memory alloys vary drastically depending on the composition of the alloy. Melton teaches that to achieve a desired transformation temperature in a nickel-titanium alloy, it is necessary to control the composition to one-tenth to one-hundredth of a percent. Melton at page 23. Because of the exacting conditions necessary to achieve a desired temperature characteristic in a shape memory alloy, a broad disclosure of a composition range, such as the 50.5% to 60% nickel concentration disclosed by Mathis, encompasses and defines a genus comprising many possible distinct compositions with each composition having greatly varying characteristics.

The Examiner does not provide any motivation or teaching to show why it would have been obvious to one skilled in the art to select the exact composition within the broad range of nickel-titanium alloys disclosed by Mathis. Moreover, the Examiner is reminded that the present claims, with the exception of claim 15, do not recite a nickel-titanium alloy. Therefore, the Examiner's assertion that it would have been obvious to one skilled in the art to select the exact nickel-titanium composition required to achieve the claimed limitations fails to establish a *prima facie* case of obviousness.

For at least the foregoing reasons, Applicant respectfully submits that Mathis does not teach or suggest the claimed invention and requests the reconsideration and withdrawal of the rejection.

### III. Conclusion

In view of the foregoing remarks, Applicant submits that this claimed invention, is neither anticipated nor rendered obvious in view of the prior art references cited against



this application. Applicant therefore requests the Examiner's reconsideration of the application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, L.L.P.



Dated: September 7, 2005

By: ADRIANNA L. BUEH REG. NO. 48,564 FOR  
Louis M. Troilo  
Reg. No. 45,284

**Attachment:** Melton, K.N., "Ni-Ti Based Shape Memory Alloys," Engineering Aspects of Shape Memory Alloys (1990), pp. 21-35.

# **Engineering Aspects of Shape Memory Alloys**

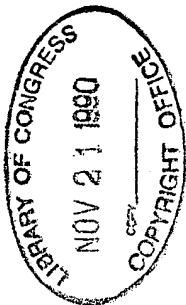
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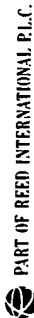
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First published 1990

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#### British Library Cataloguing in Publication Data

Engineering aspects of shape memory alloys.

1. Alloys-Shape memory effects

I. Duerig, T. W.

669.94

ISBN 0-750-61009-3

#### Library of Congress Cataloging-in-Publication Data

Engineering aspects of shape memory alloys / edited by T. W. Duerig.

p. cm.

Includes bibliographical references and index.

ISBN 0-750-61009-3

1. Alloys--Thermomechanical properties. 2. Shape memory effect.

I. Duerig, T. W.

TN690 E546 1990

669.9--dc20

90-2104

CIP

## Introduction

It has now been over 50 years since the first observations of shape memory, and over 20 years since people first began to find applications for the effect. Certainly many people believe that practical application has progressed much slower than expected: when inventive people first observe the effect they immediately begin to conjure ideas for its application, amazed that it has been known for so long by the scientific community and is yet nearly unknown to design engineers. Shape memory has even become famous as "a solution looking for a problem".

But this reputation is unfair if one considers that the entire technology is new. These are not simply new alloys of steel or titanium, but represent an entirely new philosophy of engineering and design. The most fundamental property descriptors are different: yield strength, modulus, and ductility are replaced by stress rate, recovery stress and  $M_s$ . Moreover, product designs using shape memory are generally not evolutionary, but revolutionary in nature. One can hardly expect large industries to immediately convert basic product designs to shape memory. In fact progress has been impressive. At the time of writing, it is estimated that the worldwide business in shape memory exceeds 30 million US dollars, and is growing at over 25% per year. Product diversity is also most impressive, including fine medical wires, electrical switches, eyeglass frames, appliance controllers, pipe couplings and electronic connectors.

Still, it is clear that the technology lags behind the science. The origin and mechanism of shape memory are now well understood, but many of the engineering aspects are not. The purpose of this book is to extend our understanding of shape memory by defining terms, properties and applications. It includes tutorials, overviews, and specific design examples - all written with the intention of minimizing the science and maximizing the engineering aspects. Although the individual chapters have been written by many different authors, each one of the best in their fields, the overall tone and intent of the book is not that of a proceedings, but that of a textbook. There has been a concerted editing effort to unify terms, avoid duplication, and fill gaps.

Shape memory applications can generally be divided into four categories: free recovery, constrained recovery, work production (actuators) and superelasticity. These groupings are made according to the primary function of the memory element, but are useful in defining common product screening criteria, pitfalls and engineering design parameters. We define the groups as follows:

causing some variants to form preferentially. In terms of Figure 9, the effect of these microstresses is to cause the 9c structure to form instead of the structure shown in 9b.

## 6. Summary

The shape memory effect is a consequence of a crystallographically reversible martensitic phase transformation occurring in the solid state. Although there are many ways (orientations) to produce the martensite phase from its parent during cooling, once the lower symmetry martensite is formed it has only one unique reversion path during the reverse transformation because of crystallographic restrictions. The transformation of the parent phase into martensite is basically a deformation process, but because the individual units of martensite self-accommodate, the overall macroscopic deformation upon transformation is zero. When the shape memory martensite is deformed, a particular orientation of the various self-accommodating units - that most favorably oriented with respect to the applied stress - grows at the expense of others, eventually leading to a single orientation of martensite. As before, this orientation has only one reversion path, which is the essence of the shape memory - a deformed and reoriented martensitic phase which is thermally responsive. Strains on the order of seven to ten percent are typically recoverable in this manner.

Shape memory alloys also display superelasticity, a mechanical type of shape memory as opposed to the thermally induced (by heating) shape memory described above. In this case, when the parent phase is deformed above the martensite start temperature, the martensitic transformation occurs "prematurely" because the applied stress substitutes for the thermodynamic driving force usually obtained by cooling. But since the applied stress is basically uniaxial, only one orientation (out of many) of martensite is selectively formed, and this imparts an overall deformation to the specimen. This deformation disappears when the stress is released and the original specimen shape is restored, leading to a mechanical shape memory.

Finally, a two-way shape memory can be realized in shape memory materials, whereby a specimen is programmed by means of thermomechanical treatment producing microstresses in the parent phase which in turn program the specimen to behave as a stress-induced martensitic transformation. That is, the microstresses favor only a single orientation of martensite upon subsequent cooling, which produces a spontaneous deformation. When the specimen is heated the normal one-way shape memory process occurs and its original shape is reproduced. The two-way process can be repeated indefinitely (as with a thermostat) as opposed to the one-way memory, which is a one time only operation (as in making a mechanical connection).

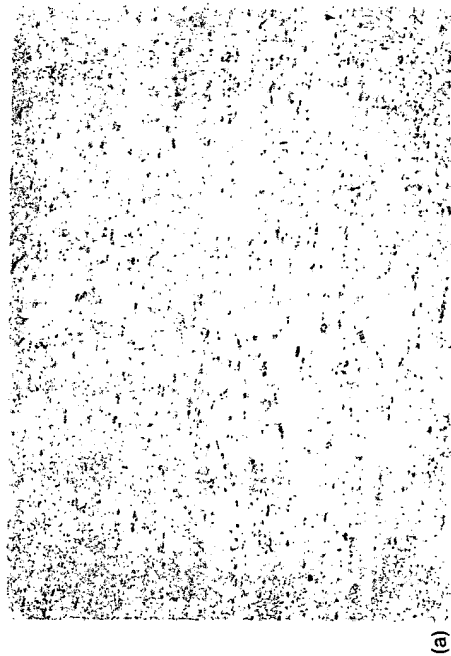
## Ni-Ti Based Shape Memory Alloys

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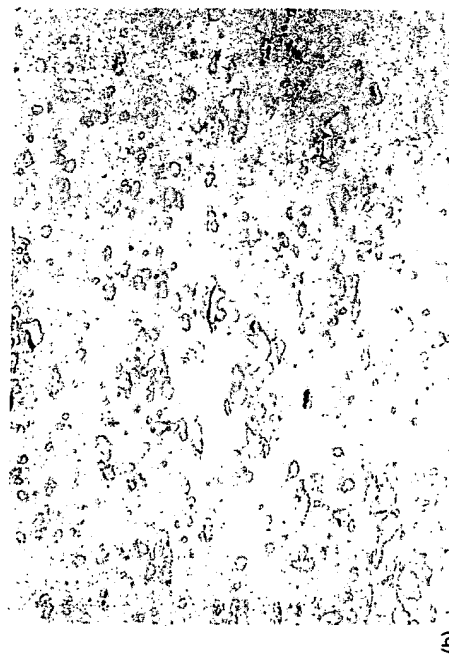
Shape memory alloys based on nickel and titanium have to date provided the best combination of material properties for most commercial applications. In fact it was the discovery in the 1960's of shape memory properties in the Ni-Ti system which led to the rapid growth of interest in the shape memory phenomenon. This discovery took place at NOL, the Naval Ordnance Laboratory and hence the acronym NITI-NOL or Nitinol which is commonly used when referring to Ni-Ti based SMA's. A series of extensive reports<sup>1-3</sup> documented the properties of Ni-Ti, mainly in wire form, and provided much useful information for the designer. However since that time there has been significant progress in the understanding of the alloy, particularly with regard to the effects of processing and heat treatment on the mechanical and shape memory behaviour. This paper is intended as an overview of the Ni-Ti SMA's, with the emphasis on some of the more recent developments.

### 1. Metallurgy of Ni-Ti Alloys

Ni-Ti SMA's are ordered intermetallic compounds based on the equiatomic composition. From the phase diagram<sup>4</sup> this compound exists as the stable phase down to room temperature. Consequently, in contrast to copper based alloys, no betatizing and quenching is necessary to prevent the decomposition into other phases at intermediate temperatures. However, at low temperatures the stoichiometric range of Ni-Ti is very narrow and so the alloys often contain precipitates of a second intermetallic phase. The microstructure is thus primarily single phase, with small amounts of other phases distributed in the matrix, Figure 1a. One factor which is often ignored in considering the microstructure of Ni-Ti alloys, is the presence of oxygen. Titanium is very reactive, particularly in the molten state, and some oxygen is invariably present in the alloy. From the Ni-Ti-O phase diagram<sup>5</sup>, oxygen decreased the stoichiometric range of the NiTi compound and can unexpectedly result in compositions within a three phase field. Thus Ni<sub>3</sub>Ti can be present for example in a titanium rich alloy. Furthermore, the oxide Ti<sub>4</sub>Ni<sub>2</sub>O is isostructural with the intermetallic Ti<sub>2</sub>Ni<sup>6</sup> which can make unique phase identification difficult. If the composition of the alloy deviates from stoichiometry, then larger precipitates are present, as can be seen in Figure 1b for a Ti-rich alloy. These larger second phase particles can have a marked effect on the hot workability of Ni-Ti, particularly on the titanium rich side where they are brittle and often result in cracking.



(a)



(b)

Figure 1: (a) The microstructure of a hot worked 50 at % Ni alloy showing a fine distribution of second phase particles, and (b) the microstructure of a hot worked 52 at % Ni alloy showing a higher volume fraction of coarser particles compared to 1a. Note some cracking resulting from hot working these brittle particles.

Within the composition range at which the Ni-Ti phase exists at ambient temperature,  $M_s$  depends quite strongly on composition, Figure 2, particularly on the Ni-rich side. Ti-rich alloys show less sensitivity, primarily as a result of the formation of a Ti-rich precipitate, leaving the matrix composition essentially the same. The composition dependence of  $M_s$  shown in Figure 2 has important practical consequences. Precise composition control is required when melting the alloys. Depending upon the desired

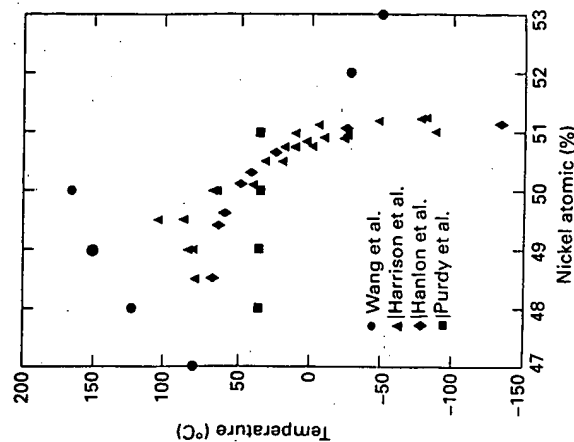


Figure 2: The dependence of the transformation temperature  $M_s$  on composition.

$M_s$ , the necessary control is to between one tenth and on hundredth of a percent! By way of comparison, the typically allowed variation in chromium content of 18/8 stainless steel is 2%. The compositional accuracy required for Ni-Ti is mostly more precise than the errors in chemical analysis. Consequently, in most cases for quality control purposes the transformation temperature itself is measured, rather than the chemical composition. As a result of this precise composition control to achieve the desired  $M_s$ , other properties such as yield strength etc show significantly smaller lot to lot variations than in most other engineering metallic materials.

Figure 2 includes data from Wang et al<sup>7</sup>, which indicates a maximum transformation temperature of around 150°C. However the results were obtained from damping experiments of a not very sophisticated kind. Bars were struck with a hammer, and the transformation temperature subjectively determined from whether the sound was a leaden thud or a ringing sound similar to a bell. Quantitative measurements showed<sup>8</sup> that the damping behaviour is in fact quite complex. Consequently the data from Wang et al<sup>7</sup> support the general trend of transformation temperature as a function of composition, but transformation temperatures in the vicinity of 150°C should not be expected.

Ni-rich alloys are unstable in the sense that  $M_s$  shifts in annealed material can occur during prolonged exposure at temperatures which could be met during service. This instability is the consequence of the formation of precipitates, and the precipitation sequence has been studied in detail<sup>9</sup>. Figure 3 shows the  $A_s$  temperature for a series of alloys in the quenched and quenched and aged conditions. It can be seen that, for Ti-rich alloys there is very little difference between these heat treat conditions, whereas Ni-rich alloys show a low  $A_s$  in the as-quenched condition, but subsequent

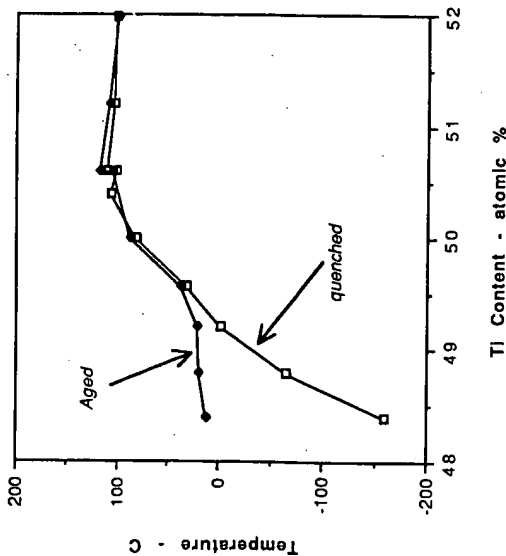


Figure 3:  $A_s$  temperatures as a function of composition for water quenched from 850°C and quenched and aged at 400°C samples.

aging can lead to a dramatic increase. On aging, the Ni-Ti decomposes into a more Ti-rich matrix composition with higher  $A_s$ , together with a Ni-rich phase finely dispersed within it.

The fact that the instability occurs on the nickel rich side only is a consequence of the solubility range of Ni-Ti extending to higher nickel contents at temperatures above around 500°C<sup>4</sup>. At high temperatures excess nickel goes into solution in Ni-Ti, and on aging for longer times at lower temperatures it precipitates out again. On the titanium rich side the solubility range is almost independent of temperature. For many applications of Ni-Ti alloys, this instability is of little importance, since service temperatures in the range where the  $M_s$  shift is rapid do not often occur. However for couplings where a cryogenic annealed alloy is used, service exposure in the 200 to 300°C range is likely to raise  $M_s$  above the minimum operating temperature, rendering the coupling useless.

## 2. Mechanical Properties

Like most SMA's, Ni-Ti alloys show marked differences in mechanical behavior depending on whether they are tested in the austenitic or the martensitic phases. The stress-strain curve of the martensite can be divided into three well defined regions<sup>10-13</sup>, see Figure 4. An initial low plateau results from the stress induced growth of one martensite orientation at the expense of an adjacent, unfavourably oriented one, this process occurring by a detwinning type of mechanism. At higher stresses there is a second region which is usually linear, although not purely elastic. It is believed<sup>13</sup> that the deformation mechanism in this stage is a mixture of elastic deformation of the detwinned martensite, together with the formation of new orientations of martensite

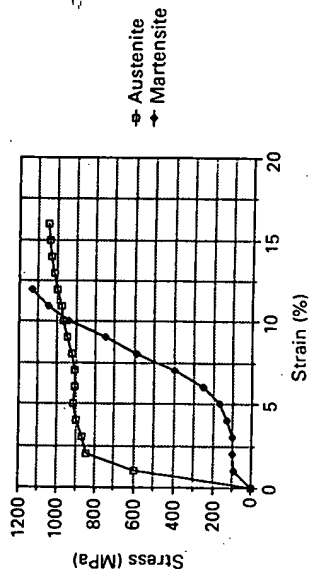


Figure 4: The stress-strain curves of a Ni-Ti-10% Cu alloy in the austenitic and martensitic conditions.

which intersect those already present, and which provide additional heat recoverable strain.

The transition to the third region is a result of the onset of irreversible plastic deformation, as in the case of the yielding of all conventional metals. Thus the maximum amount of heat recoverable or memory strain is obtained by initially deforming to the end of stage two. If larger deformation strains are used, then the reversible martensitic deformation processes and the dislocations resulting from plastic flow interact and the memory strain decreases, see below.

The length of the martensitic plateau in the stress-strain curve extends typically to around 5-6%. However, depending on the details of the alloy and particularly its prior thermo-mechanical history, this "plateau" can vary from a continuous curve with an inflection point to a clear horizontal plateau with a sharp yield point and upturn. Because of this variation in yield behavior, many have found it more useful to use a 1% strain offset than a 0.2% offset when defining a yield stress. Furthermore, for wrought material the shape of the stress strain curve depends on orientation. Figure 5

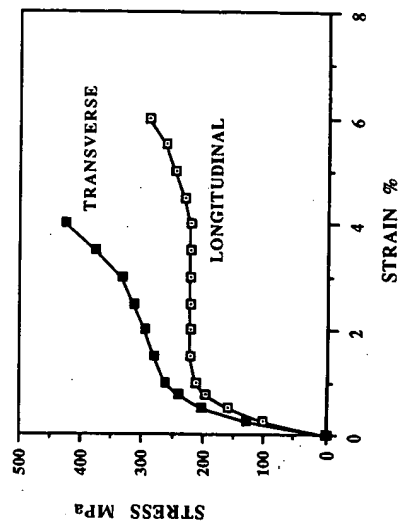


Figure 5: Martensitic stress strain curves of specimens taken longitudinally and transversely from rolled sheet.

shows curves from rolled sheet, where it can be seen that testing in the longitudinal direction results in a well defined plateau, whereas in the transverse direction none exists and the stress levels are much higher. The details of the martensite curve depend also on the mode of deformation, marked differences can be obtained in tension, compression and torsion<sup>14</sup>, see Figure 6.

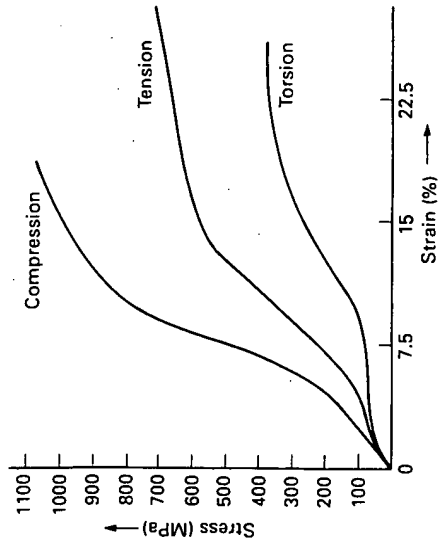


Figure 6: Stress strain curves for a Ni-Ti-10% Cu alloy measured in compression, tension and torsion.

The length of the martensite plateau also determines the strain at which the transition to region III of the stress strain curve occurs, and can therefore affect the amount of memory strain. Thus although it is often stated that up to 8% strain is heat recoverable, the actual amount depends on the alloy, its thermo-mechanical processing, testing direction and deformation mode. In many cases, a conservative design would use less than 8% strain.

For test temperatures just above  $M_s$ , and where this temperature is reached by cooling, the alloy is austenitic at the start of the test and the mechanism of yielding is the onset of stress induced martensite. As the test temperature is increased, the deformation mode stays the same, but the martensite is thermodynamically less stable and so a greater stress is required to induce its formation (as discussed in the previous chapter). Between  $M_s$  and  $M_d$  the yield stress (to induce martensite) increases linearly with temperature, the slope being given by the Clausius-Clapyron equation. A plot of initial yield stress vs temperature Figure 7, can be divided into three regions depending on the deformation temperature  $T_d$ .

$$\begin{array}{ll} T_d < M_s & \text{detwinning of martensite} \\ M_s < T_d < M_d & \text{stress induced martensite} \\ T_d > M_d & \text{plastic deformation} \end{array}$$

Figure 7 shows the data for two Ni-Ti alloys, illustrating also the general trend that as the nickel content of the alloy decreases (and thus  $M_s$  increases) the austenitic yield strength decreases.

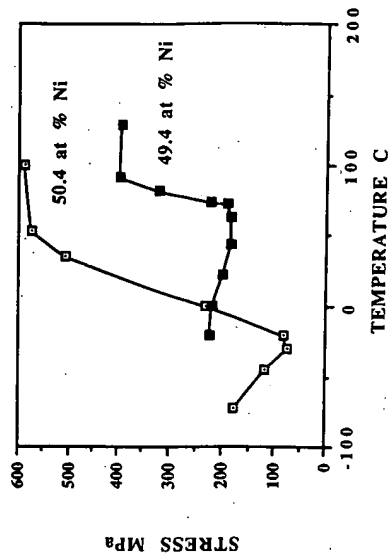


Figure 7: Yield stress measured at different temperatures for two Ni-Ti compositions. Each data point represents a separate specimen.

Methods of determining transformation temperatures will be discussed in detail in a later chapter. However one method is to thermally cycle a specimen under load, producing a curve similar to that illustrated in Figure 8. The transformation temperatures are conveniently obtained by the intersection of tangents, as shown. Ni-Ti based alloys have a hysteresis width of typically 30-50°C. Transformation

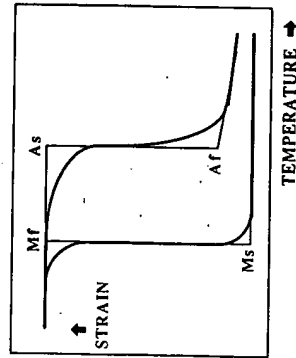


Figure 8: A schematic plot of strain versus temperature of a sample which is loaded in the austenitic condition, and then cooled and reheated through the transformation at constant load.

temperatures increase with increasing load in a linear fashion, Figure 9, the slope being thermodynamically controlled by the stress rate:  $d\sigma/dT$  (the same as that of the yield stress vs temperature plot in the testing temperature range between  $M_s$  and  $M_d$ , Figure 7). This slope, as well as being of thermodynamic significance, is also important to bear in mind when choosing an alloy for a particular application. For

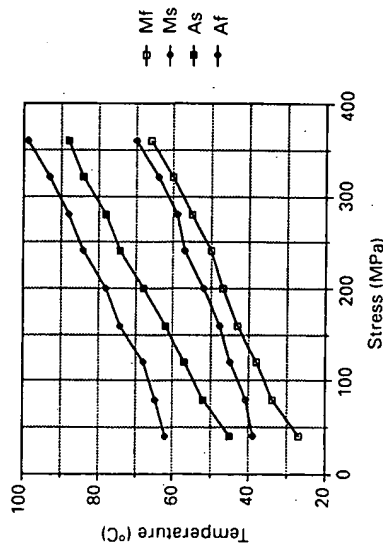


Figure 9: The transformation temperatures of a Ni-Ti-10% Cu alloy measured as a function of load by the method indicated in Figure 8.

example, both the response temperature ( $A_s$ ) and reset temperature ( $M_s$ ) of an SMA actuator will depend on the opposing force. Furthermore, for applications where the SMA is required to maintain its mechanical integrity (couplings, fasteners etc) the stress in the component can decrease on cooling below  $M_d$ . The stress rate of Ni-Ti can also change significantly from alloy to alloy, covering a range from 2.5 MPa/°C to over 15 MPa/°C. Generally alloys with lower transformation temperatures have lower stress rates, dictated by the Clausius-Clapeyron equation and a decreasing latent heat of transformation. Higher strength alloys also seem to have generally higher stress rates.

The mechanical design of a structure will often use modulus as a parameter. However for shape memory alloys in general and Ni-Ti alloys in particular, the concept of modulus is not straightforward. Figure 10 shows the Young's modulus measured dynamically<sup>15</sup> of three Ni-Ti based alloys plotted as a function of temperature, where it can be seen that dramatic changes take place. In particular, there can be a pronounced modulus decrease in the austenitic phase on cooling, which occurs before  $M_s$ . Another complicating factor concerning modulus is that the slope of the elastic loading and unloading lines are not the same, and the unloading "line" is often not in fact linear. These points can be seen from the austenitic curve shown in Figure 11. For the case of deformation of the martensite, the unloading behaviour shows considerable departure from linearity. For deformation strains above 8% the dislocations introduced can act as pinning centers for martensite twin boundaries. When the external stress is removed the dislocations move back to a new equilibrium position and take the twin boundary with them, giving much more unloading strain than normal alloys. Figure 12 shows that for a total deformation strain of 20%, only around 15% plastic strain is introduced, in other words a springback of 5% is obtained. However for 10% total strain, the plastic value is around 9%, indicating only 1% springback.

### 3. Effects of Thermo-mechanical Processing

In 1965, four years after the alloy patent on binary Ni-Ti was filed<sup>16</sup>, a process patent was filed claiming cold working in the martensite as a way of increasing the yield

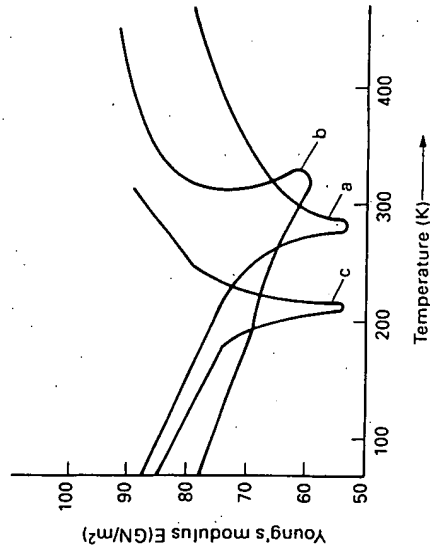


Figure 10: The dynamic Young's modulus of three Ni-Ti based alloys as a function of temperature, from reference 15.

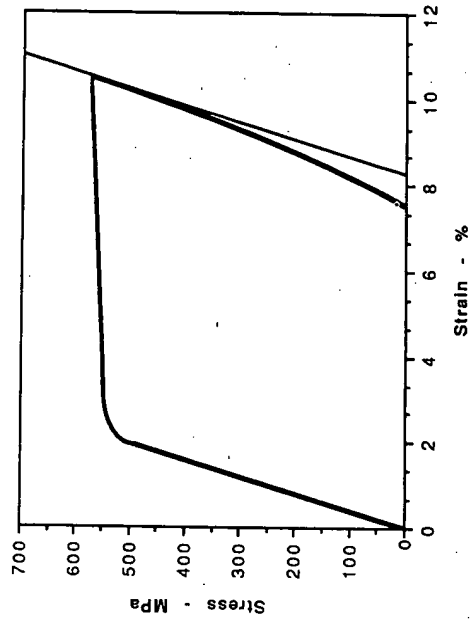


Figure 11: The loading and unloading stress strain behavior of a Ni-Ti alloy tested in the austenitic condition.

strength of the alloy<sup>17</sup>. Since that time the combination of cold work in the martensite together with a subsequent anneal has been extensively explored as a way of improving the SMA characteristics. Cold work alone, i.e. without the annealing step, destroys the martensitic plateau on the stress-strain curve. Thus a material cold worked 20% in the martensite has a very



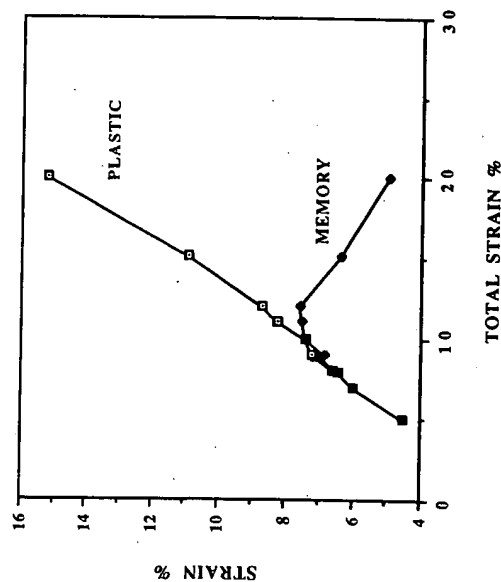


Figure 12: The plastic and shape memory strains of a Ni-Ti alloy plotted as a function of total strain.

high yield strength<sup>18</sup>, but its shape memory properties are poor in that only very low recoverable strains are possible. Annealing will restore the memory effect, but decrease the yield stress. The choice of amount of cold work and the actual annealing temperature dictate the trade off in these two properties. It is believed that cold work introduces a high density of "random" dislocations, which impede the mobility of the twin boundaries. Annealing rearranges these dislocations into cells of relatively dislocation free areas within which the martensite twins can be mobile, but surrounded by dislocation networks. It is the presence of the cells or subboundaries which gives the hardening.

Figure 13 shows the effect on austenitic yield strength of annealing temperature after 40% cold work in the martensite of a 50.6 at %Ni alloy. It can be seen that a rapid decrease is observed in the range 350 to 450°C, followed by a more gradual decrease out to 850°C. At the same time,  $M_s$  increases, Figure 14, and again the increase is rapid between 350 and 450°C. Comparing Figures 13 and 14 it is apparent that for a given alloy, although processing can increase the yield strength, it is done at the expense of a lower  $M_s$ .

One of the principal improvements of Ni-Ti alloy properties obtained by processing is cyclic behaviour. Figure 15 shows the strain measured as a function of temperature of the same binary alloy annealed at 850°C, with a load corresponding to an initial stress of 150 MPa being applied. The main thing to notice is the large amnesia of around 1.5%, in other words a single memory cycle with this stress leads to an irreversible deformation of 1.5%. Doing the same test after cold working 40% and annealing at 400°C results in amnesia of around 0.5% Figure 16. The strain obtained on cooling and the amnesia on heating are plotted in Figures 17 and 18 as a function of stress after cold working and annealing at 350°C and 450°C respectively. The 350°C anneal results in a very small amnesia for stresses up to 300 MPa, whereas the 450°C anneal

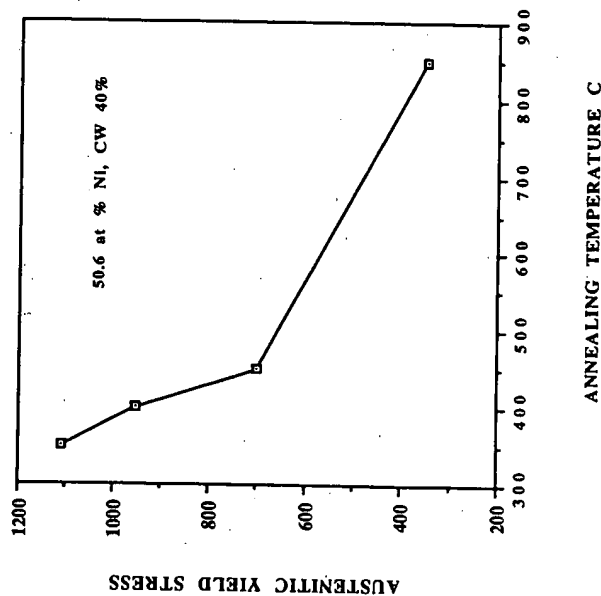


Figure 13: The austenitic yield stress of a 50.6 at.%Ni alloy, cold worked and then annealed for 30 mins. at the temperatures indicated.

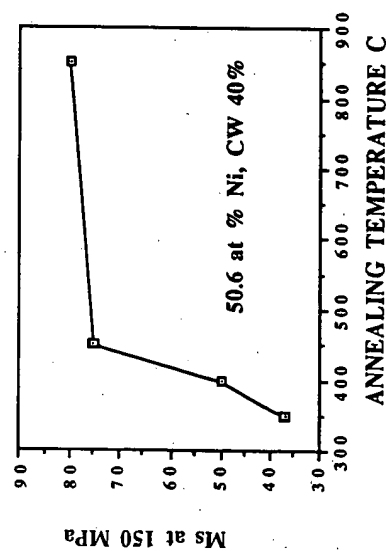


Figure 14: The transformation temperature  $M_s$  (measured at 150MPa) as a function of annealing temperature for the same alloy used in Figure 13.

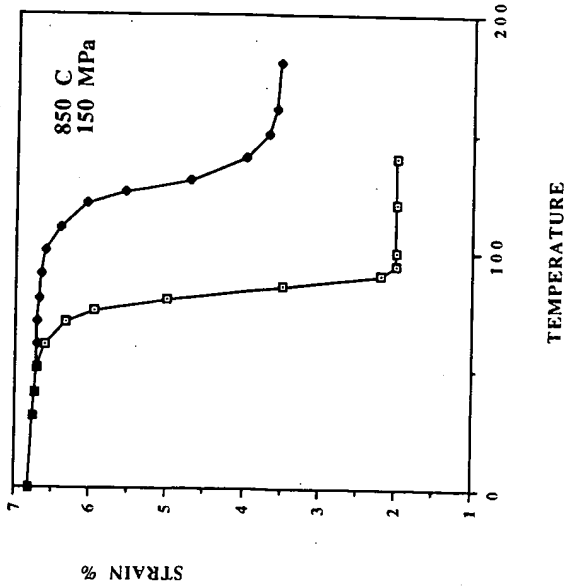


Figure 15: Strain versus temperature curves at 150 MPa for a 50.6 at.%Ni alloy annealed at 850°C.

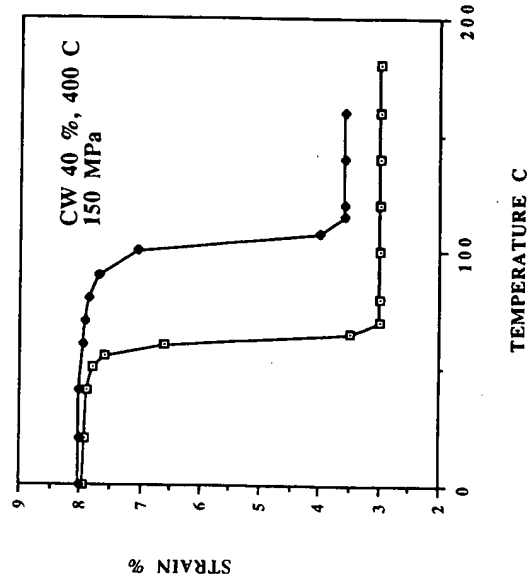


Figure 16: Strain versus temperature curves at 150 MPa for the same alloy as Figure 15, but cold worked 40% and annealed at 400°C.

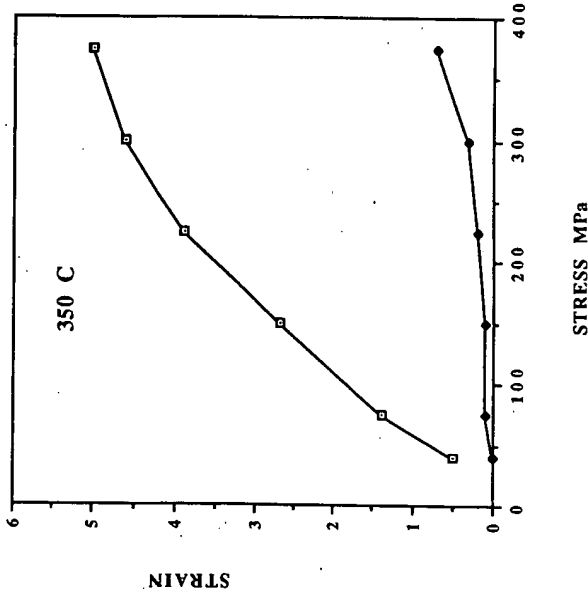


Figure 17: The strain obtained on cooling (upper curve) and the amnesia (lower curve) as a function of stress for a Ni-Ti alloy cold worked 40% and annealed at 350°C.

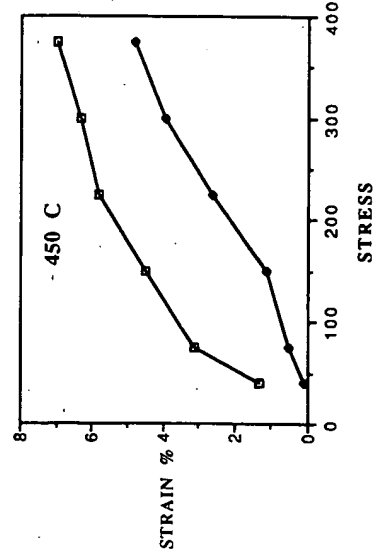


Figure 18: The data of Figure 17 after annealing at 450°C

gives significant amnesia at all useful working stress levels. For low temperature anneals where the amnesia is low, the data obtained from the first cycle, as shown here, approximates the cyclic behaviour after many cycles. However where the amnesia on the first cycle is high, the cyclic stability is so poor that ratcheting or walking occurs, in other words the strain end points shift with increasing cycles.

When choosing a Ni-Ti alloy for an actuator type of application, it must be remembered that for a given composition, a high  $M_s$  temperature is obtained by annealing out any effects of prior cold work. The cyclic stability is therefore poor. Devices triggering at or above 100°C are unlikely to have mechanical stability over tens of thousands of cycles. However, it should be remembered that this is a *mechanical* instability, where the strain per cycle varies at high working loads. There is no *metallurgical* instability leading to shifts in the response temperature as a result of prolonged exposure around 100°C, in contrast to Cu-based SMA's.

Thermo-mechanical processing is important for the optimization of pseudoelastic behaviour. Increasing the yield strength of the austenite can widen the temperature range over which martensite can be stress induced without the intervention of plastic deformation. This will be discussed in detail in a later Chapter. From a mechanistic point of view however, the binary superelastic alloy is more complicated. If superelastic behaviour at ambient temperature is required, then  $M_s$  will be lower and the alloy will tend to be nickel rich. Solution treatment followed by rapid cooling and cold working will provide additional hardening from the precipitation of nickel rich phases as a result of the instabilities discussed above.

#### 4. Corrosion Behavior

In the galvanic series, Ni-Ti based alloys as a family are slightly more noble than 316 stainless steel, and show similar corrosion behaviour. The excellent corrosion resistance is provided by a naturally formed thin adherent oxide layer known as a passive film. This film is very stable, so the Ni-Ti alloys are resistant to many forms of corrosive attack. However in some aggressive conditions such as highly acidified chloride solutions, breakdown of this passive film can occur. Such corrosive environments are very severe for most engineering materials; nevertheless if Ni-Ti is to be used in these conditions, some form of protective coating is advisable.

Electrochemical measurements show Ni-Ti based alloys have a good resistance to pitting in a chloride environment<sup>19,20</sup>. However data obtained from a scratch test indicated that the healing of the passive film may be a difficult and relatively slow process<sup>20,21</sup>.

Compared with other commercially available SMA's, Ni-Ti is by far the most corrosion resistant. For most applications in the actuator, electrical connector and fastener fields, Ni-Ti has a superior corrosion behaviour than the other components of the assembly. In the case of coupling applications, the corrosion resistance is more than adequate except in severe conditions, where protection is advisable. As a general rule, if no corrosion protection of the tubes or pipes is deemed necessary, none is required of the Ni-Ti coupling used to join them.

#### 5. Effect of Alloying Elements

The addition of third or fourth elements to Ni-Ti provide a powerful tool for controlling the properties, and can be used to:

- control transformation temperatures
- increase the stability of  $M_s$  with respect to thermal history
- control the hysteresis width
- increase austenitic strength
- reduce or increase martensitic strength

- improve corrosion resistance
- suppress the R-phase

Some of the additions giving particularly useful combinations of properties are copper, niobium, and precious metals. These form the subject of separate chapters in this book.

For applications requiring  $M_s$  to be below room temperature, binary alloys show instability or an  $M_s$  dependence on prior thermal history. Furthermore they tend to have poor ductility. Alloying elements such as Fe, Co or Cr which are known to depress  $M_s$  and substitute primarily for Ni<sup>3, 21, 22</sup>, can be used as additions to an approximately 50 at % Ti alloy. In this range, (Figure 2) the sensitivity of  $M_s$  to Ni/Ti ratio variations is relatively low, but the  $M_s$  value corresponding to this plateau is lowered by the third element.

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